Supporting Information

‘Honeycomb’ nanotube assembly based on thiacalix[4]arene derivatives by weak interactions

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<table>
<thead>
<tr>
<th>Atoms involved D−H···A</th>
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<th>D···A</th>
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<table>
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<th>Compound</th>
<th>Type</th>
<th>S···Cg</th>
<th>Symmetry</th>
<th>r/Å</th>
<th>d/Å</th>
<th>α/α’(°)</th>
<th>φ(°)</th>
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<td>III</td>
<td>S(2)···Cg(2)</td>
<td>1/3+x-y, 1/3+x, 2/3-z</td>
<td>4.194</td>
<td>3.463</td>
<td>177.33/74.41</td>
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<td></td>
<td>S(2)···Cg(3)</td>
<td>1/3+x-y, 1/3+x, 5/3-z</td>
<td>4.104</td>
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<td>72.62/157.94</td>
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<tr>
<td></td>
<td>III</td>
<td>S(14)···Cg(1)</td>
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<td>4.250</td>
<td>3.727</td>
<td>75.15/156.22</td>
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<td>S(14)···Cg(4)</td>
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<td>4.241</td>
<td>3.546</td>
<td>172.37/69.70</td>
<td>51.49</td>
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The parameter values of \( r, d, \alpha, \alpha' \), and \( \phi \) lie in the allowable range of S···π interactions.\(^{31}\)

**Reference**

Figure S2
Space filling view of the triply helical nanotube motif are found in the crystal structure of five compounds. Side view showing helical nature of strands coloured yellow, red and blue. Other molecular components omitted for clarity.
Figure S3 The C-H⋯O interactions are found in the packing between neighbouring hexameric discs of $7\cdot\text{CHCl}_3$. The green dotted lines represent C-H⋯O interactions. Hydrogen atoms (except for those involved in hydrogen bonding) and CHCl$_3$ molecules not involved in omitted for clarity.
Figure S4 View along the crystallographic $b$ axis, the intermolecular C-H···O, C-H···π and S···π interactions are green, violet and gray dot lines, respectively, observed in the triply helical nanotubes of 8. Hydrogen atoms (except for those involved in hydrogen bonding) are omitted for clarity.
Figure S5

(A) View along the crystallographic b axis, the intermolecular C-H···O, C-H···π and S···π interactions are green, violet and gray dot lines, respectively, observed in the triply helical nanotubes of 9a and 9b.

(B) The C-H···O interactions observed in neighbouring nanotubes of 9b. C-H···O interactions shown as dashed green lines.

Hydrogen atoms (except for those involved in hydrogen bonding) are omitted for clarity.
Figure S6

(A) Schematic of the structure of 10.

(B) The S···π interactions and π···π interactions observed in hexameric disc.

(C) Non-covalent interactions the same layer neighbouring hexameric of 10·H₂O observed in 2D network.

(D) The different layer neighbouring hexameric of 10·H₂O observed in 3D network.

(E) Non-covalent interactions the adjacent layer neighbouring hexameric of 10·H₂O observed in 3D network.

C-H···O interactions, C-H···π interactions, and S···π interactions are green, violet and gray dot lines, respectively. Hydrogen atoms (except for those involved in hydrogen bonding) and H₂O are omitted for clarity.
Figure S7 View along the crystallographic $b$ axis, the intermolecular C-H···O and S···π interactions are green and gray dot lines, respectively, observed in the triply helical nanotubes of 11. Hydrogen atoms (except for those involved in hydrogen bonding) are omitted for clarity.
Figure S8 Schematic representations of Type I, Type II, and $X_3$ synthon halogen···halogen contacts. The angles: Type I ($\theta_1=\theta_2=140–180^\circ$) and Type II ($\theta_1=150–180^\circ$, $\theta_2=90–120^\circ$). The $X_3$ synthon is a trigonal array of halogen atoms with attractive electrophile-nucleophile Type II contacts.
Figure S9

(A) The intermolecular S···π interactions are gray dot lines observed in the triply helical nanotubes of 12-CHCl₃.
(B) Structure of 12-CHCl₃ showing hexameric discs through the C-H···π interactions. C-H···π interactions shown as dashed orange lines.
Figure S10 $^1$HNMR and ESI – MS of compound 7
Figure S11 $^1$HNMR and ESI – MS of compound 12
<table>
<thead>
<tr>
<th>Compound</th>
<th>Plane AR (°)</th>
<th>Plane BR (°)</th>
<th>Plane CR (°)</th>
<th>Plane DR (°)</th>
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<td>70.34</td>
<td>35.71</td>
<td>71.19</td>
<td>30.57</td>
</tr>
<tr>
<td>7-CHCl₃</td>
<td>71.09(68.14)</td>
<td>33.52(30.60)</td>
<td>73.51(76.51)</td>
<td>37.89(38.77)</td>
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<td>8</td>
<td>77.15</td>
<td>32.69</td>
<td>65.91</td>
<td>44.37</td>
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<td>9</td>
<td>75.11</td>
<td>43.26</td>
<td>69.95</td>
<td>38.63</td>
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<td>10-H₂O</td>
<td>110.16</td>
<td>20.73</td>
<td>109.25</td>
<td>28.42</td>
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<td>11</td>
<td>78.60(80.25)</td>
<td>89.92(89.43)</td>
<td>73.46(70.94)</td>
<td>43.25(35.64)</td>
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<tr>
<td>12-CHCl₃</td>
<td>68.73</td>
<td>43.97</td>
<td>68.73</td>
<td>43.97</td>
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()) represents the disordered molecular

<table>
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<tr>
<th>Compound</th>
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<th>Plane BD (°)</th>
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<td>109.6(110.63)</td>
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<td>102.97</td>
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<td>27.98(29.39)</td>
<td>46.84(52.80)</td>
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<td>12-CHCl₃</td>
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<td>92.06</td>
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()) represents the disordered molecular
Table S3 The three types of S···π interactions in compounds 7-12 and their metric parameters

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<th>Compound</th>
<th>Type</th>
<th>S···Cg</th>
<th>Symmetry</th>
<th>r / Å</th>
<th>d / Å</th>
<th>α / α’ (°)</th>
<th>φ (°)</th>
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<tbody>
<tr>
<td>7·CHCl₃</td>
<td>III</td>
<td>S(2)···Cg(1) (1/3+x-y, -1/3+x, 2/3-z)</td>
<td>4.357</td>
<td>C(6)</td>
<td>3.820</td>
<td>74.72/154.99</td>
<td>58.52</td>
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<td>S(2)···Cg(4) (1/3+x-y, -1/3+x, 5/3-z)</td>
<td>4.150</td>
<td>C(30)</td>
<td>3.599</td>
<td>168.48/71.26</td>
<td>57.52</td>
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<td>8</td>
<td>III</td>
<td>S(2)···Cg(3) (1+y, 1-x+y, 2-z)</td>
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<td>C(21)</td>
<td>3.701</td>
<td>165.26/61.41</td>
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<td>S(2)···Cg(4) (1+y, 1-x+y, 1-z)</td>
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<td>C(26)</td>
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<td>III</td>
<td>S(1)···Cg(3) (1/3+y, 2/3-x+y, -1/3-z)</td>
<td>4.152</td>
<td>C(20)</td>
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<td>175.33/74.07</td>
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<td>S(1)···Cg(4) (1/3+y, 2/3-x+y, 2/3-z)</td>
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<td>C(28)</td>
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<td>69.63/159.33</td>
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<td>10·H₂O</td>
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<td>C(5)</td>
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<td>118.0/83.91</td>
<td>38.51</td>
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<td>S(2)···Cg(6) (4/3+x-y, -2/3-x, -1/3+z)</td>
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<td>C(36)</td>
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<td>102.66/87.08</td>
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<tr>
<td>11</td>
<td>II</td>
<td>S(1)···Cg(3) (1+y, 1-x+y, 1-z)</td>
<td>4.106</td>
<td>C(16)</td>
<td>3.664</td>
<td>58.79/135.44</td>
<td>62.44</td>
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<td>S(3)···Cg(4) (1+y, 1-x+y, -z)</td>
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<td>C(22)</td>
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<tr>
<td>12·CHCl₃</td>
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<td>S(2)···Cg(1) (-x+y, y, 1/2+z)</td>
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<td>C(5)</td>
<td>3.394</td>
<td>129.52/104.0</td>
<td>69.57</td>
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<td>S(4)···Cg(2) (x, y, 1+z)</td>
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<td>C(10)</td>
<td>3.376</td>
<td>111.79/124.14</td>
<td>42.87</td>
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Table S4 \( \pi \cdots \pi \) interactions for five compounds

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<th>Compound</th>
<th>Cg(I)···Cg(J)</th>
<th>Symmetry</th>
<th>( \alpha )</th>
<th>Cg···Cg</th>
<th>Cg(I)_Perp</th>
<th>Cg(J)_Perp</th>
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<tbody>
<tr>
<td>7∙CHCl₃</td>
<td>Cg(1)···Cg(1)</td>
<td>1-x,-y,1-z</td>
<td>0</td>
<td>4.050(3)</td>
<td>3.446(2)</td>
<td>3.447(2)</td>
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<td>Cg(4)···Cg(4)</td>
<td>-x+5/3,-y+1/3,-z+4/3</td>
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<td>4.047(2)</td>
<td>3.468(1)</td>
<td>3.468(1)</td>
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<tr>
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<td>Cg(2)···Cg(2)</td>
<td>-x+1,-y,-z</td>
<td>0</td>
<td>4.708(3)</td>
<td>3.431(2)</td>
<td>3.431(2)</td>
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<tr>
<td>10∙H₂O</td>
<td>Cg(3)···Cg(4)</td>
<td>1+y,1-x-y,-z</td>
<td>0</td>
<td>3.725(3)</td>
<td>28.216(5)</td>
<td>3.513(2)</td>
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<td>Cg(5)···Cg(5)</td>
<td>5/3-x,1/3-y,1/3-z</td>
<td>0</td>
<td>4.801(5)</td>
<td>-3.323(3)</td>
<td>-3.323(3)</td>
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<tr>
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<td>Cg(4)···Cg(4)</td>
<td>-x+4/3,-y+5/3,-z+5/3</td>
<td>0</td>
<td>4.300(4)</td>
<td>-3.509(2)</td>
<td>-3.509(2)</td>
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Table S5 C-H···\( \pi \) interactions for six compounds

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<tr>
<th>Compound</th>
<th>Atoms involved C-H···Cg</th>
<th>Symmetry</th>
<th>H···Cg</th>
<th>C···Cg</th>
<th>( \angle )C-H···Cg</th>
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<tbody>
<tr>
<td>7∙CHCl₃</td>
<td>C(3) - H(3)···Cg(2)</td>
<td>1-x, -y, 1-z</td>
<td>3.183</td>
<td>4.064(4)</td>
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<td>C(4) - H(4A)···Cg(3)</td>
<td>1-x, -y, 1-z</td>
<td>3.179</td>
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<td>126.1</td>
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<td>C(5) - H(5)···Cg(4)</td>
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<td>4.007(1)</td>
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<td>C(7) - H(7A)···Cg(2)</td>
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<td>3.520(7)</td>
<td>132.6</td>
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<td>C(23) - H(23A)···Cg(4)</td>
<td>1/3-x-y, -1/3+x, 5/3-z</td>
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<td>3.790(10)</td>
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<td>C(23) - H(23A)···Cg(5)</td>
<td>1/3+x-y, -1/3+x, 5/3-z</td>
<td>2.93</td>
<td>3.43(3)</td>
<td>134.0</td>
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<td>C(13) - H(13)···Cg(1)</td>
<td>1/3+y, 2/3-x+y, 2/3-z</td>
<td>3.138</td>
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<td>C(30) - H(30)···Cg(1)</td>
<td>x-y, x-1, -z+1</td>
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<td>C(15') - H(15B)···Cg(3)</td>
<td>1/3+y, 2/3-x+y, -1/3-z</td>
<td>2.96</td>
<td>3.89(3)</td>
<td>161.0</td>
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<td>C(32') - H(32A)···Cg(1)</td>
<td>1/3+x-y, -1/3+x, 2/3-z</td>
<td>2.92</td>
<td>3.77(5)</td>
<td>147.0</td>
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<td>C(15) - H(15C)···Cg(3)</td>
<td>1/3+y, 2/3-x+y, -1/3-z</td>
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<td>3.64(2)</td>
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<td>C(32) - H(32C)···Cg(1)</td>
<td>1/3+x-y, -1/3+x, 2/3-z</td>
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<td>3.61(2)</td>
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<td>10∙H₂O</td>
<td>C(38) - H(38)···Cg(1)</td>
<td>1-x, -y, 1-z</td>
<td>3.113</td>
<td>4.041(5)</td>
<td>175.9</td>
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<td>C(24) - H(24)···Cg(1)</td>
<td>-x+4/3,-y+5/3,-z+5/3</td>
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<td>3.476(9)</td>
<td>148.0</td>
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<td>C(25) - H(25)···Cg(2)</td>
<td>-x+4/3,-y+5/3,-z+5/3</td>
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<td>3.442(6)</td>
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<td>C(25') - H(25')···Cg(2)</td>
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<td>12∙CHCl₃</td>
<td>C(13) - H(13B)···Cg(2)</td>
<td>-x+ y, y, -1/2+z</td>
<td>2.84</td>
<td>3.682(6)</td>
<td>146.6</td>
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Table S6 O···π interactions in compounds 9, 10-H$_2$O and 11

<table>
<thead>
<tr>
<th>Compound</th>
<th>C–O (C=O)···Cg</th>
<th>Symmetry</th>
<th>r/ Å</th>
<th>d/ Å</th>
<th>α(°)</th>
<th>φ(°)</th>
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<td>C(14) - O(4)···Cg(2)</td>
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<td>C(12)</td>
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<td>C(14) - O(4)···Cg(3)</td>
<td>1-x, -y, -z</td>
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<td>C(23)</td>
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<td>1-x, -y, -z</td>
<td>3.213(15)</td>
<td>C(25) - C(26)</td>
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<td>102.0</td>
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<td>C(14) - O(4A)···Cg(1)</td>
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Table S9 Hydrogen bonds of compound 9

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## Table S10 Hydrogen bonds of compound 10·H₂O

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## Table S11 Hydrogen bonds of compound 11

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<td>2.19</td>
<td>2.985(6)</td>
<td>163.6(3)</td>
</tr>
<tr>
<td>O(1) - H(1)···O(7')</td>
<td></td>
<td>2.28</td>
<td>3.040(16)</td>
<td>155.0(1)</td>
</tr>
</tbody>
</table>
### Table S12 Hydrogen bonds of compound 12-CHCl₃

<table>
<thead>
<tr>
<th>Atoms involved D - H···A</th>
<th>Symmetry</th>
<th>H···A</th>
<th>D···A</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(2) - H(2)···S(2)</td>
<td></td>
<td>2.61</td>
<td>3.059(7)</td>
<td>114.8</td>
</tr>
<tr>
<td>O(2) - H(2)···O(1)</td>
<td></td>
<td>2.31</td>
<td>2.810(8)</td>
<td>119.6</td>
</tr>
</tbody>
</table>

### Table S13 The Cl···Cl interactions of compound 12-CHCl₃

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>d(Cl···Cl)/Å</th>
<th>d(C···Cl)/Å</th>
<th>𝜃₁ = 𝜃₂(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(17) - Cl(2)···Cl(2) - C(17)</td>
<td>1-x, 2-y, -z</td>
<td>2.921</td>
<td>4.492</td>
</tr>
</tbody>
</table>

### Table S14 The cyano···Cl interactions of compound 12-CHCl₃

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>d(N···Cl)/Å</th>
<th>d(Cα···Cl) /Å</th>
<th>d(Cβ···N) /Å</th>
<th>𝜃₁(°)</th>
<th>𝜃₂(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cα - N(1)···Cl(3) - Cβ</td>
<td>x-y, x, 2-z</td>
<td>2.779</td>
<td>3.786</td>
<td>4.285</td>
<td>147.94</td>
</tr>
</tbody>
</table>

### Table S15 The Cl···π interactions of compound 12-CHCl₃

<table>
<thead>
<tr>
<th>C - Cl···Cg</th>
<th>Symmetry</th>
<th>r/ Å</th>
<th>d/ Å</th>
<th>α(°)</th>
<th>φ(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(17) - Cl (1)···Cg(1)</td>
<td>y, 1-x+y, 1-z</td>
<td>3.403(6)</td>
<td>C(1) - C(6)</td>
<td>3.470</td>
<td>104.52(12)</td>
</tr>
<tr>
<td>C(17) - Cl (1)···Cg(2)</td>
<td>x, 1+x-y, -1/2+z</td>
<td>3.928(3)</td>
<td>C(7)</td>
<td>3.448</td>
<td>106.87(10)</td>
</tr>
</tbody>
</table>
**Table S16** Sums of the van der Waals radii (vdW) of C and phenyl ring with common lp-containing atoms (atom LP)\(^{S2}\)

<table>
<thead>
<tr>
<th>Atom LP</th>
<th>vdW radii/ Å</th>
<th>vdW(LP) + vdW(C(^a))/ Å</th>
<th>vdW(LP) + vdW(Phenyl ring)/ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.20</td>
<td>2.90</td>
<td>3.05</td>
</tr>
<tr>
<td>O</td>
<td>1.52</td>
<td>3.22</td>
<td>3.37</td>
</tr>
<tr>
<td>Cl</td>
<td>1.75</td>
<td>3.40</td>
<td>3.45</td>
</tr>
<tr>
<td>S</td>
<td>1.80</td>
<td>3.50</td>
<td>3.65</td>
</tr>
<tr>
<td>N</td>
<td>1.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(^a)</td>
<td>1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenyl ring(^{S3})</td>
<td>1.85</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Reference**
<table>
<thead>
<tr>
<th>Compound</th>
<th>Split atoms</th>
<th>Occupation factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-CHCl₃</td>
<td>C(26)-C(31), S(3), O(4)/C(26')-C(31'), S(3'), O(4')</td>
<td>0.859(16)/0.141(16)</td>
</tr>
<tr>
<td>8</td>
<td>C(14)-C(16)/C(14')-C(16')</td>
<td>0.826(8)/0.174(8)</td>
</tr>
<tr>
<td>9</td>
<td>C(15)-C(17)/C(15')-C(17') &lt;br&gt; C(32)-C(34)/C(32')-C(34')</td>
<td>0.66/0.34 &lt;br&gt; 0.75/0.25</td>
</tr>
<tr>
<td></td>
<td>O(4), O(4A)/O(4B), O(2)/O(2')</td>
<td>0.375, 0.375/0.25 &lt;br&gt; 0.69/0.31</td>
</tr>
<tr>
<td></td>
<td>O(6)/O(6')</td>
<td>0.78/0.22</td>
</tr>
<tr>
<td>11</td>
<td>C(15)-C(30), S(2), S(3), S(4), O(5), O(6), O(7') &lt;br&gt; C(15')-C(30'), S(2'), S(3'), S(4'), O(5'), O(6'), O(7')</td>
<td>0.707(3)/0.293(3)</td>
</tr>
</tbody>
</table>